(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 288 970 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
05.03.2003 Bulletin 2003/10

(51) Int Cl.7: H01B 7/295, H01B 7/28,
C08K 3/22

(21) Application number: 01121137.2

(22) Date of filing: 04.09.2001

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR
Designated Extension States:
AL LT LV MK RO SI

(71) Applicant: PIRELLI CAVI E SISTEMI S.p.A.
20126 Milano (IT)

(72) Inventors:
- Tirelli, Diego
20099 Sesto San Giovanni (MI) (IT)
- Martinotto, Luca
20025 Legnano (MI) (IT)
- Pelizzoni, Andrea
20030 Seveso (MI) (IT)
- Peruzzotti, Franco
20025 Legnano (MI) (IT)
- Albizzati, Enrico
28040 Lesa (NO) (IT)

(74) Representative: Bottero, Carlo et al
Pirelli S.p.A.,
Direz. Proprieta' Industriale,
Viale Sarca 222
20126 Milano (IT)

(54) Self-extinguishing cable and flame-retardant composition used therein

(57) A self-extinguishing cable and the flame-retardant composition used therein are disclosed. The cable comprises at least one flame-retardant coating comprising a) at least one polymer material; b) at least one inorganic hydrated flame-retardant filler; and c) at least one silane substituted with at least one C_{10}-C_{40} hydrocarbon group and with at least one hydrolysable group. The self-extinguishing cable shows improved insulating properties in water or in the presence of a moist environment without adversely affecting self-extinguishing properties.

Printed by Jouve, 75001 PARIS (FR)

Description

[0001] The present invention concerns a self-extinguishing cable and the flame-retardant composition used therein. In particular, the invention relates to a self-extinguishing cable having improved insulating properties and to the flame-retardant composition used therein.

[0002] Self-extinguishing cables are generally produced by extruding over the core of the cable a flame-retardant coating consisting of a polymer composition which has been given flame retardant properties by the addition of a suitable additive. Polyolefin-based compositions comprising, for example, polyethylene or ethylene/vinyl acetate copolymers, containing an organic halide combined with antimony trioxide as flame-retardant additive can, for example, be used for this purpose. However, halogenated flame-retardant additives have many drawbacks since they partially decompose during processing of the polymer, giving rise to halogenated gases which are toxic to workers and corrode the metal parts of the polymer-processing equipment. In addition, when they are placed directly in a flame, their combustion gives rise to very large amounts of fumes containing toxic gases. Similar drawbacks are encountered when polyvinyl chloride (PVC) with added antimony trioxide is used as base polymer.

[0003] Thus, in recent years, use has been made of halogen-free compositions in the production of self-extinguishing cables, in which a polymer base, generally of polyolefin type, is mixed with inorganic flame-retardant fillers, generally hydroxides, hydrated oxides or hydrated salts of metals, in particular of aluminium or magnesium, such as magnesium hydroxide or alumina trihydrate, or mixtures thereof (see, for example, patents US 4,145,404, US 4,673,620, EP-B-328,051 and EP-B-530,940).

[0004] Inorganic flame-retardant fillers, generally hydroxides as above noted, can be used as they are or coated with various hydrophobic products since they are usually strongly hygroscopic and this tendency to absorb water, even at the operating conditions of the cable, can cause the loss of the electric insulating characteristics of the coating material; therefore, to reduce hygroscopicity, hydrophobic agents are advantageously used to coat the flame-retardant filler.

[0005] Among hydrophobic agents, saturated or unsaturated fatty acids or the salts thereof, in particular oleic, stearic or isostearic acid and the corresponding oleates or stearates, etc. with e.g. zinc, magnesium or aluminium, etc.; or organic silanes such as short chain alkyl- and alkylalkoxy-silanes, or titanium, aluminium and zirconium organic compounds, are known.

[0006] For example, WO 96/27885 describes a flame-retardant composition for coating electrical cables, comprising polypropylene as polymer matrix supplemented with 1-20% by weight of a polyethylene wax and 100-200% by weight of magnesium hydroxide coated with a hydrophobic product, for example an alkylsilane. This coating is said to increase the compatibility between the filler and the polymer matrix and at the same time to impart hydrophobic properties to the flame-retardant coating, thus avoiding the absorption of moisture which would reduce the efficiency of the insulating properties of the material.

[0007] EP-A-0249010 describes thermoplastic mouldings compounds having high impact strength and high elongation at break, with good fire performance, which are based on polymer blends consisting of a mixture of 1 to 40% by weight of propylene homo- and/or co-polymer, from 0.5 to 5% by weight of ethylene-propylene-diene terpolymer rubber and from 40 to 70% by weight of silane coated magnesium hydroxide and, optionally, polyethylene, polyacrylic ester and polyvinyl acetate homo- and co-polymer.

[0008] JP-5-17692 and JP-7-161230 disclose a flame retardant composition endowed with either improved acid resistance or suppressed hygroscopicity, respectively, comprising magnesium hydroxide processed with a surface-treatment agent containing at least one compound selected from fatty acids and the metal salts thereof, silane and titanate coupling agents, the composition being added to a plastic or rubber and being used as a coating material on halogen-free self-extinguishing electric wires and cables.

[0009] EP-A-0568488 discloses particulate magnesium hydroxide suitable for use as a flame-retardant additive for a polymer, especially for wires and cables, having peculiar BET surface area and average particle size. Optionally, the particulate magnesium hydroxide may be coated with an agent selected from a fatty acid, a carboxylated unsaturated polymer, an organosilane, e.g. 3-aminopropyltriethoxysilane or vinyl-tris(2-methoxy-ethoxy)silane, an organotitanate or a salt thereof. The articles formed by mixing particulate magnesium hydroxide with a polymer are said to exhibit optimal properties including flame-retardant effectiveness, tensile strength and percent elongation as well as the dispersability of the particulate magnesium hydroxide in the polymer material.

[0010] WO 99/05688 discloses a low smoke, self-extinguishing cable and a halogen-free flame retardant coating used therein wherein natural magnesium hydroxide is used as flame-retardant filler. The coating comprises- (a) a crystalline propylene homopolymer or copolymer; (b) a copolymer of ethylene with at least one α-olefin, and optionally with a diene, having a Composition Distribution Index (CDI) greater than 45%; (c) natural magnesium hydroxide. To improve compatibility between magnesium hydroxide and the polymer material, a coupling agent, such as saturated silane compounds or silane compounds containing at least one ethylenic unsaturation, epoxides containing an ethylenic unsaturation, monocarboxylic acids or dicarboxylic acids having at least one ethylenic unsaturation, or derivatives thereof, f.i. anhydrides or esters, may be added to the coating composition. The cable thus obtained exhibits enhanced

flexibility, thermocompression resistance and flame-retardant properties.

[0011] WO 00/39810 discloses a process for producing self-extinguishing low smoke cables wherein the flame-retardant coating layer is obtained by extruding a flame-retardant composition comprising a polymer base, such as polyethylene, polypropylene, copolymers of ethylene or propylene with α-olefins, copolymers of ethylene with at least one ester chosen from alkyl acrylates, alkyl methacrylates and vinyl carboxylates, natural rubber, butyl rubber or mixtures thereof, an inorganic flame-retardant filler such as hydroxides, hydrated oxides, salts or hydrated salts of calcium, aluminium or magnesium and a dehydrating agent, such as calcium oxide and zeolites. The resulting flame-retardant layer is smooth and uniform and substantially free of pores and succeeds in ameliorating the mechanical properties of the coating. A coupling agent, capable of increasing the interaction between the active groups of the flame-retardant filler and the polymer chains, may be added in order to enhance the compatibility between the filler and the polymer base. This coupling agent can be, for example, a saturated silane compound or a silane compound containing at least one ethylenic insaturation, for instance vinyltris(2-methoxyethoxy)silane.

[0012] WO 00/19452 discloses a low smoke, self-extinguishing electrical cable coated with a flame-retardant composition, comprising (a) an ethylene homopolymer or copolymer with an α-olefin or with an ethylenically unsaturated ester, having a density of from 0.905 to 0.970 g/cm^3; (b) a copolymer of ethylene with at least one α-olefin, and optionally with a diene, having a density of from 0.860 to 0.904 g/cm^3 and a Composition Distribution Index (CDI) greater than 45%; and (c) natural magnesium hydroxide in an amount such as to impart flame-retardant properties; wherein at least one of the polymeric components (a) and (b) contains hydrolyzable organic silane groups grafted onto the polymer chain in order to effectively compatibilize said components with the magnesium hydroxide. The resulting cable shows good tensile properties with excellent flexibility.

[0013] Self-extinguishing cables as those described above are usually tested and used in alternating current. Quality control tests in alternating current include measuring the variation of the insulating constant (Ki) after having subjected the cable to an ageing treatment in water at the working temperature.

[0014] Unexpectedly, the Applicant has found that common flame retardant coatings which show positive results in ageing tests in water performed in alternating current do not give equally good performances when subjected to analogous ageing tests in water carried out in direct current.

[0015] The Applicant has realised that the use of conventional hydrophobic agents, such as fatty acids or short chain silanes, in halogen-free flame retardant compositions gives unsatisfactory results when it is requested to produce self-extinguishing cables able to pass ageing tests in water, particularly in salt containing water, performed in direct current. Such tests are of outstanding importance for some applications where the cables are operated in direct current, such as in the railway field.

[0016] Therefore, the Applicant has faced the technical problem of how to produce cables with a flame-retardant, halogen-free coating showing enhanced insulating properties in water or in the presence of a moist environment, not only in alternating current but also in direct current, without adversely affecting self-extinguishing properties.

[0017] The Applicant has now found that it is possible to solve the above problem by adding a peculiar organosilane to a flame-retardant composition comprising a polymer base and an inorganic flame-retardant filler as described hereinunder.

[0018] In a first aspect, the present invention thus relates to a self-extinguishing cable comprising at least one conductor and at least one flame-retardant coating, wherein the at least one flame-retardant coating comprises:

a) at least one polymer material selected from: olefin homopolymers, olefin copolymers, copolymers of at least one olefin with at least one ethylenically unsaturated ester, polyesters, polyethers, polyether/polyester copolymers, and mixtures thereof;

b) at least one inorganic hydrated flame-retardant filler;

c) at least one silane substituted with at least one C_{10}-C_{40} hydrocarbon group and with at least one hydrolysable group.

[0019] Preferably, the polymer material in the flame-retardant coating of the self-extinguishing cable of the invention is selected from: polyethylene; copolymers of ethylene with at least one α-olefin containing from 3 to 12 carbon atoms, and optionally with at least one diene containing from 4 to 20 carbon atoms; polypropylene; thermoplastic copolymers of propylene with ethylene and/or at least one α-olefin containing from 4 to 12 carbon atoms; copolymers of ethylene with at least one ester selected from alkyl acrylates, alkyl methacrylates and vinyl carboxylates, wherein the alkyl and the carboxylic groups comprised therein are linear or branched, and wherein the linear or branched alkyl group may contain from 1 to 8, preferably from 1 to 4, carbon atoms, while the linear or branched carboxylic group may contain from 2 to 8, preferably from 2 to 5, carbon atoms; and mixtures thereof.

[0020] With "α-olefin" it is generally meant an olefin of formula CH_2=CH-R, wherein R is a linear or branched alkyl having from 1 to 10 carbon atoms. The α-olefin can be selected, for example, from propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-dodecene and the like. Among them, propylene, 1-butene, 1-hexene and

1-octene are particularly preferred.

[0021] With "diene" it is generally meant:

a linear, conjugated or non-conjugated diolefin having from 4 to 20 carbon atoms, for example 1,3-butadiene, 1,4-hexadiene or 1,6-octadiene;

a monocyclic or polycyclic diene having from 4 to 20 carbon atoms, for example 1,4-cyclohexadiene, 5-ethylidene-2-norbornene, 5-methylene-2-norbornene, 5-vinyl-2-norbornene.

[0022] More preferably, the polymer material is selected from copolymers of ethylene with at least -one α-olefin containing from 3 to 12 carbon atoms, and optionally with at least one diene containing from 4 to 20 carbon atoms, obtained by single-site catalysis.

[0023] Preferably, the inorganic hydrated flame-retardant filler is selected from: metal hydroxides, hydrated metal oxides, metal salts having at least one hydroxyl group, and hydrated metal salts; particularly, the flame-retardant filler is a calcium, aluminium, magnesium or zinc hydroxide, hydrated oxide, salt having at least one hydroxyl group or hydrated salt.

[0024] In the flame-retardant coating of the self-extinguishing cable of the invention, the C_{10}-C_{40} hydrocarbon group contained in the silane is preferably a C_{10}-C_{40}, more preferably C_{12}-C_{24}, alkyl, alkenyl, aryl, alkylaryl, arylalkyl, arylalkenyl, alkenylaryl group, whereas the hydrolysable group is preferably a C_1-C_{16} alkoxy group, optionally substituted by at least one C_1-C_{16} alkoxy group.

[0025] According to a preferred embodiment, the silane may have the following formula:

$$Y_{4-(x+z)}SiR_xR'_z \qquad (I)$$

wherein:

x is 1, 2 or 3; z is zero, 1 or 2; with the proviso that x+z is not higher than 3;

Y, equal or different from each other, are C_1-C_8, preferably C_1-C_4, alkoxy groups, optionally substituted by at least one C_1-C_8, preferably C_1-C_4, alkoxy group;

R, equal or different from each other, are selected from:

C_{10}-C_{40}, preferably C_{12}-C_{24}, more preferably C_{14}-C_{20} alkyl groups, optionally substituted by at least one C_6-C_{14} aryl group;

C_{10}-C_{40}, preferably C_{12}-C_{24}, more preferably C_{14}-C_{20} alkenyl groups, optionally substituted by at least one C_6-C_{14} aryl group;

C_6-C_{14}, preferably C_6-C_{10}, aryl groups, optionally substituted by at least one C_1-C_{30} alkyl group and/or by at least one C_2-C_{30} alkenyl group;

with the proviso that each of R has from 10 to 40 carbon atoms;

R', equal or different from each other, are selected from:

hydrogen;

C_1-C_{20}, preferably C_1-C_{16}, more preferably C_1-C_{12} alkyl groups, optionally substituted by at least one C_6-C_{14} aryl group;

C_2-C_{20}, preferably C_2-C_{16}, more preferably C_2-C_{12} alkenyl groups, optionally substituted by at least one C_6-C_{14} aryl group;

C_6-C_{14} aryl groups, optionally substituted by at least one C_1-C_{20} alkyl group and/or by at least one C_2-C_{20} alkenyl group.

[0026] According to a particularly preferred embodiment, in formula (I) x is 1; z is zero; Y, equal or different from each other, are selected from C_1-C_4 alkoxy group, optionally substituted by at least one C_1-C_4 alkoxy group, f.i. methoxy, ethoxy or methoxyethoxy group; R is a C_{14}-C_{20} alkyl, f.i. hexadecyl or octadecyl group.

[0027] In a second aspect, the present invention concerns a flame-retardant composition comprising:

a) at least one polymer material selected from: olefin homopolymers, olefin copolymers, copolymers of at least one olefin with at least one ethylenically unsaturated ester, polyesters, polyethers, polyether/polyester copolymers, and mixtures thereof;

b) at least one inorganic hydrated flame-retardant filler;

c) at least one silane substituted with at least one C_{10}-C_{40} hydrocarbon group and with at least one hydrolysable group.

[0028] Examples of polymer materials that may be used in the self-extinguishing cables and flame-retardant compositions of the invention are: high-density polyethylene (HDPE) (d=0.940-0.970 g/cm^3), medium-density polyethylene (MDPE) (d=0.926-0.940 g/cm^3), low-density polyethylene (LDPE) (d=0.910-0.926 g/cm^3); linear low-density polyethylene (LLDPE) and ultra-low-density polyethylene _ (ULDPE) (d=0.860-0.910 g/cm^3); polypropylene (PP); thermoplastic copolymers of propylene with ethylene; ethylene/vinyl acetate (EVA) copolymers; ethylene/ethyl acrylate (EEA) copolymers, ethylene/butyl acrylate (EBA) copolymers; ethylene/α-olefin rubbers, in particular ethylene/propylene rubbers (EPR), ethylene/propylene/diene rubbers (EPDM); and mixtures thereof.

[0029] Copolymers which are particularly preferred are those which can be obtained by copolymerization of ethylene with at least one α-olefin containing from 3 to 12 carbon atoms, and optionally with at least one diene, in the presence of a single-site catalyst, in particular a metallocene catalyst or a constrained geometry catalyst. These copolymers are characterized by a density of between 0.860 and 0.904 g/cm^3, preferably from 0.865 to 0.902 g/cm^3, and by a Composition Distribution Index (CDI) greater than 45%, said index being defined as the percentage by weight of the copolymer molecules having an α-olefin content of up to 50% of the total average molar content of α-olefin. These copolymers preferably have the following monomer composition: 75-97 mol%, preferably 90-95 mol%, of ethylene; 3-25 mol%, preferably 5-10 mol%, of α-olefin; 0-5 mol%, preferably 0-2 mol%, of a diene. The α-olefin is preferably selected from propylene, 1-butene, 1-hexene, 1-octene and the like. Products of this type are commercially available under the tradenames Engage® from Du Pont-Dow Elastomers and Exact® from Exxon Chemical.

[0030] The ethylene copolymers obtained by single-site catalysis are preferably used as a mixture with a crystalline propylene homopolymer or copolymer, as described, for example, in the above mentioned WO 99/05688, or with an ethylene homopolymer or copolymer which has a density of between 0.905 and 0.970 g/cm^3, preferably between 0.910 and 0.940 g/cm^3, as described, for example, in WO 00/19452 or, alternatively, in US patent 5,707,732. In particular, the polymer material preferably comprises from 5 to 60% by weight, more preferably from 10 to 45% by weight, of a propylene or ethylene homopolymer or copolymer as defined above, and from 40 to 95% by weight, more preferably from 55 to 90% by weight, of an ethylene copolymer obtained by single-site catalysis as defined above, the percentages being relative to the total weight of the polymeric components.

[0031] Examples of inorganic hydrated flame-retardant fillers which may be used in the self-extinguishing cables and flame-retardant compositions of the invention are: magnesium hydroxide, alumina trihydrate, hydrated magnesium carbonate, hydrated calcium, magnesium carbonate, $4ZnO.B_2O_3.H_2O$, $2ZnO.3B_2O_3.3.5H_2O$, or mixtures thereof. Magnesium hydroxide is particularly preferred, since it is characterized by a decomposition temperature of about 340°C and thus allows high extrusion temperatures to be used. It is more particularly preferred to use magnesium hydroxide of natural origin, obtained by grinding minerals based on magnesium hydroxide, such as brucite or the like, as described in WO 99/05688.

[0032] The flame-retardant filler is generally used in the form of particles which are untreated or surface-treated with saturated or unsaturated fatty acids containing from 8 to 24 carbon atoms, or metal salts thereof, such as, for example: oleic acid, palmitic acid, stearic acid, isostearic acid, lauric acid; magnesium or zinc stearate or oleate; and the like. In order to increase the compatibility with the polymer material, the flame-retardant filler can likewise be surface-treated with suitable coupling agents, for example short chain organic silanes or titanates such as vinyltriethoxysilane, vinyltriacetylsilane, tetraisopropyl titanate, tetra-n-butyl titanate and the like.

[0033] The amount of flame-retardant filler to be added is predetermined so as to obtain a cable which is capable of passing flame/fire-propagation tests, particularly those according to standard IEC 332-1 or IEC 332-3 A,B,C. In general, this amount is between 10 and 90% by weight, preferably between 30 and 80% by weight, relative to the total weight of the flame-retardant composition.

[0034] The silanes above defined as component c) of the flame-retardant coating of the cable of the invention are preferably in an amount from 0.1% to 10%, preferably 0.5% to 5% by weight with respect to the total weight of the inorganic flame-retardant filler. Examples of silanes which are suitable for the cable and composition of the invention are: hexadecyltrimethoxysilane, hexadecyltriethoxysilane, octadecyltrimethoxysilane and octadecyltriethoxysilane.

[0035] A coupling agent capable of increasing the interaction between the active hydroxyl groups of the flame-retardant filler and the polymer chains may be added to the mixture in order to enhance the compatibility between the flame-retardant filler and the polymer material. This coupling agent can be selected from those known in the art, for example: short chain saturated silane compounds or silane compounds containing at least one ethylenic unsaturation; epoxides containing an ethylenic unsaturation; monocarboxylic acids or, preferably, dicarboxylic acids having at least one ethylenic unsaturation, or derivatives thereof, in particular anhydrides or esters.

[0036] Examples of short chain silane compounds which are suitable for this purpose are: γ-methacryloxypropyltrimethoxysilane, allyltrimethoxysilane, allyltriethoxysilane, allylmethyldimethoxysilane, allylmethyl-diethoxysilane, methyltriethoxysilane, methyltris (2-methoxyethoxy)silane, dimethyldiethoxysilane, vinyltris (2-methoxyethoxy)silane, vinyltrimethoxysilane, vinyl methyldimethoxysilane, vinyltriethoxysilane, octyl triethoxysilane, isobutyltriethoxysilane, isobutyl trimethoxysilane and the like, or mixtures thereof.

[0037] Examples of epoxides containing an ethylenic unsaturation are: glycidyl acrylate, glycidyl methacrylate,

monoglycidyl ester of itaconic acid, glycidyl ester of maleic acid, vinyl glycidyl ether, allyl glycidyl ether and the like, or mixtures thereof.

[0038] Monocarboxylic or dicarboxylic acids, having at least one ethylenic unsaturation, or derivatives thereof, which can be used as coupling agents are, for example: maleic acid, maleic anhydride, fumaric acid, citraconic acid, itaconic acid, acrylic acid, methacrylic acid and the like, and anhydrides or esters derived from these, or mixtures thereof. Maleic anhydride is particularly preferred.

[0039] The coupling agents can be used as they are or pre-grafted onto a polyolefin, for example polyethylene or copolymers of ethylene with an α-olefin, by means of a radical reaction (see for example EP-A-530,940). The amount of pre-grafted coupling agent is generally between 0.05 and 5 parts by weight, preferably between 0.1 and 2 parts by weight, relative to 100 parts by weight of polyolefin. Polyolefins pre-grafted with maleic anhydride are available as commercial products known, for example, under the brand names Fusabond® (Du Pont), Orevac® (Elf Atochem), Exxelor® (Exxon Chemical), Yparex® (DSM), etc.

[0040] Alternatively, the coupling agents of carboxylic or epoxide type mentioned above (for example maleic anhydride) or the short chain silanes with ethylenic unsaturation (for example vinyltrimethoxysilane) can be added to the mixture in combination with a radical initiator so as to graft the compatibilizing agent directly onto the polymer material. An organic peroxide such as tert-butyl perbenzoate, dicumyl peroxide, benzoyl peroxide, di-tert-butyl peroxide and the like, can, for example, be used as initiator. This method is described, for example, in patent US-4,317,765, in Japanese patent application JP-62-58774 or alternatively in the above mentioned WO 99/05688 and WO 00/19452.

[0041] The amount of coupling agent to be added to the mixture can vary mainly depending on the type of coupling agent used and on the amount of flame-retardant filler added, and is generally between 0.01 and 5%, preferably between 0.05 and 2%, by weight relative to the total weight of the polymer material mixture.

[0042] Conventional antioxidants which are suitable for this purpose are, for example:

polymerized trimethyldihydroquinoline, 4,4'-thiobis (3-methyl-6-tert-butyl)phenol; pentaerythryl tetra-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], 2,2'-thiodiethylene bis[3-(3,5-di-tert-butyl-4-hydroxy-phenyl)propionate] and the like, or mixtures thereof.

[0043] Other fillers which may be used in the present invention include, for example, glass particles, glass fibres, calcined kaolin, talc and the like, or mixtures thereof. Processing co-adjuvants usually added to the polymer material are, for example, calcium stearate, zinc stearate, stearic acid, paraffin wax, silicone rubbers and the like, or mixtures thereof. Another component that may be added to the flame-retardant composition and cables according to the present invention is at least one dehydrating agent, such as calcium oxide or a zeolite, generally in an amount of from 0.5 to 15% by weight with respect to the weight of the flame retardant filler, as described in the above-mentioned patent application WO 00/39810.

[0044] The flame-retardant compositions according to the present invention are preferably used in non-crosslinked form, in order to obtain a coating with thermoplastic properties which is thus recyclable.

[0045] The flame-retardant compositions according to the present invention can be prepared by mixing the components a), b) and c) as above defined together with the other additives which may be present according to techniques known in the art, for example using an internal mixer of the type containing tangential rotors (Banbury) or interpenetrating rotors, or in continuous mixers of the Ko-Kneader (Buss) type or of the co-rotating or counterrotating twin-screw type.

[0046] As an alternative, the flame-retardant compositions of the invention can be prepared by treating component b) with component c) as above defined and then mixing the resulting mixture with component a) as above defined.

[0047] As a further alternative, rather than adding the component c) as above defined during the phase of preparation of the flame-retardant composition, it can be added during the deposition by extrusion of the flame-retardant coating to produce the cable, for example via the extruder hopper or by injection into the extruder cylinder.

[0048] The component c) as above defined may be added to the flame-retardant composition as such (usually in the form of a liquid), or supported on a solid inert carrier, or also predispersed in a polymer material, such as one of those described above as component a).

[0049] During the extrusion phase, the flame-retardant compositions thus obtained can be used to coat the conductor directly, or to make an outer sheath on the conductor which has been precoated with an insulating layer. When two layers are present, the extrusion can take place in two separate phases, the inner layer being extruded on the conductor in a first passage and the outer layer being extruded on the inner layer in a second passage. Advantageously, the coating process can take place in a single passage, for example by means of the "tandem" technique, in which two separate extruders arranged in series are used, or alternatively by co-extrusion with a single extrusion head.

[0050] The temperature at which the flame-retardant composition is extruded can vary within a wide range and is predetermined as a function of the extrusion rate to be obtained. The extrusion rate in fact depends on the viscosity of the composition in the molten state and thus on its temperature. In turn, the viscosity depends mainly on the type

of polymer material and on the type and amount of flame-retardant filler used. The minimum extrusion temperature for the composition is generally not less than the plasticization temperature of the polymer material, while the maximum extrusion temperature is predetermined so as to avoid degradation or decomposition of the polymer material and/or of the flame-retardant filler. Thus, on the basis of the abovementioned criteria, in the case of flame-retardant compositions based on a mixture of polypropylene and ethylene/α-olefin copolymers as described above, in which magnesium-hydroxide is used as flame-retardant filler, the temperature at which the flame-retardant composition is extruded is generally between 160°C and 320°C, preferably between 200°C and 280°C.

[0051] Some examples of embodiments will now be reported for the purpose of illustrating the present invention more clearly, with particular reference to the accompanying drawings, in which:

- Figure 1 is a cross-section of a low voltage cable of the unipolar type according to the invention;
- Figure 2 is a cross-section of another low voltage cable of the unipolar type according to the invention;
- Figure 3 is a cross-section of a low voltage cable of the tripolar type according to the invention.

[0052] "Low voltage" generally means a voltage lower than 5 kV, preferably lower than 2 kV, more preferably lower than 1 kV.

[0053] With reference to Figure 1, a self-extinguishing cable (1) of the unipolar type, in particular for low voltage electric energy distribution, comprises: a conductor (2), an inner layer having electric insulating function (3) and an outer layer (4) having the function of a protective sheath with flame retardant properties consisting of the composition according to the present invention.

[0054] The inner layer (3) can be made of a polymer material, either cross-linked or non cross-linked, preferably halogen-free, having electric insulation properties. The polymer material can be selected, for instance, from: polyolefins, (omopolymers or copolymers of different olefins), copolymers ethylene/unsaturated esters, polyesters, polyethers, copolymers polyethers/polyesters, and mixtures thereof. Examples of such polymers are: polyethylene (PE), particularly linear low density PE (LLDPE); polypropylene (PP); thermoplastic copolymers propylene/ethylene; elastomeric copolymers ethylenepropylene (EPR) or ethylene-propylene-diene (EPDM); copolymers ethylene/vinylacetate (EVA); copolymers ethylene/methylacrylate (EMA); copolymers ethylene/ethylacrylate (EEA); copolymers ethylene/butylacrylate (EBA); copolymers ethylene/alpha-olefin, and the like. The inner layer (3) may also be a flame-retardant coating obtained e.g. from a flame-retardant composition according to the present invention.

[0055] Alternatively, referring to Figure 2, a self-extinguishing cable (1) of the unipolar type, particularly for the distribution of low voltage electric energy, can be made of a conductor (2) directly coated with the flame-retardant composition above described so as to form an outer layer (4) having flame retardant properties, without interposing other insulating layers. In this way, the outer layer (4) works also as electric insulation layer.

[0056] A thin polymer layer (not shown in the figures) having an antiabrasive function may also be externally applied. A pigment may be added to the material forming the outer layer (4) or the antiabrasive layer in order to provide the cable with a specific colouring for identification purposes. Alternatively, the cable can be identified by a thin coloured strip which may be applied externally.

[0057] With reference to Figure 3, a self-extinguishing cable (1) of the tripolar type, in particular for the distribution of low voltage electric energy, comprises three conductors (2), each one coated with an insulating layer (3), two of which being the phase conductors, one being the neutral conductor. The insulating layers (3) may consist of an insulating polymer material selected from the ones above indicated. Alternatively, the insulating layers (3) may consist of a common flame retardant composition, or even of a flame retardant composition according to the present invention. The so insulated three conductors (2) are stranded together and the interstices among one conductor and the other are filled with a material (5), preferably having flame retardant properties as well, so as to form a continuous structure having a substantially cylindrical form. An external sheath (6) comprising the flame retardant composition according to the invention is then applied on such a structure.

[0058] Figures 1-3 show only some possible embodiments of a cable according to the invention. It is evident that suitable modifications known in the art can be made in those embodiments, but without departing from the scope of the invention. In particular, the flame retardant composition of the invention can also be advantageously used for coating telecommunications or data transmission cables, , including optical fibre cables, or even mixed energy/telecommunications cables.

[0059] The following examples are given to illustrate the invention without limiting it.

EXAMPLE 1

[0060] Some accelerated ageing tests in water containing dissolved NaCl were carried out on cable specimens as described hereinbelow.

[0061] The following flame-retardant composition was used as a reference (hereinafter: the reference mixture):

85 phr Engage® 8003 - ethylene-octene copolymer obtained by single-site catalysis (Du Pont-Dow Elastomers);
210 phr Hydrofy® G 1.5 - natural magnesium hydroxide, obtained by grinding brucite, not surface-treated (NUOVA SIMA);
0.40 phr Luperox® DC40 - peroxidic initiator: dicumyl peroxide (Atofina);
2.10 phr Silquest® A-172 - coupling agent: vinyltris(2-methoxyethoxy)silane (VTMOEO) (Witco);
15 phr Moplen® EP1X35F - random crystalline propyleneethylene copolymer: d = 0.900 g/cm^3; MFI = 9.0 g/10'; T_{2m} = 154°C; ΔH_{2m} = 90.6 J/g (Basell);
0.8 phr Irganox® 1010 - antioxidant: pentaerythryl tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] (Ciba-Geigy);
0.3 phr Irganox® MD1024 - metal deactivator: 1,2-bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamoyl)hydrazine (Ciba-Geigy) ;
6.10 phr Kezadol® GR - calcium oxide predispersed in semicrystalline EPR rubber (80% by weight of CaO), in the form of granules with average diameter 6-7 μm (Kettlitz).

[0062] The amounts of the various components are expressed as phr (parts by weight per 100 parts by weight of polymer material).

[0063] The above reference mixture was supplemented with hydrophobic additives as reported in Table 1 (the amounts of additives are expressed as % by weight with respect to the weight of flame retardant filler). The above flame-retardant compositions were prepared by using a Banbury mixer and then deposited by means of a Bandera 45 extruder onto a copper conductor having a 1.5 mm^2 section, to obtain a cable having a flame-retardant coating of 0.7 mm thickness.

[0064] Two separate tests in direct current were carried out on the so obtained cables according to the conditions illustrated herebelow:

(1) cables immersed in a 10 g/l NaCl solution at 60°C; negative pole connected to conductors, positive pole inside the solution; 3 kV direct current, applied for 5 minutes with 2 h intervals.
(2) cables immersed in a 10 g/l NaCl solution at 60°C; negative pole connected to conductors, positive pole inside the solution; 1 kV direct current, applied for 30 minutes with 12 h intervals.

[0065] The time (in hours) after which the cables shortcircuited is reported in Table 1 [t_1 for test (1) and t_2 for test (2)].

TABLE 1

SAMPLE	t_1 (h)	t_2 (h)
REF. MIX.*	72	20
1*	120	26
2	216	50
3*	120	28

REF. MIX. = reference mixture;
1 = REF. MIX. + 2% by weight of stearic acid;
2 = REF. MIX. + 2% by weight of Dynasylan® 9116 (esadecyltrimethoxy silane) ;
3 = REF. MIX. + 2% by weight of KR TTS (isopropyltriisostearyl titanate).

* = comparative

[0066] The results reported in Table 1 show that the time needed to short-circuit the cable specimens changes by varying the test conditions, the performance of cable 2 being remarkably better than that of cables 1 and 3.

EXAMPLE 2

[0067] The test in direct current applying a voltage of 1 kV for 30 minutes every 12 hours, which is closer to the operation conditions of a cable, was repeated using for the flame-retardant coating the same reference mixture of Example 1, by changing either the amount of added VTMOEO or by adding different hydrophobic additives as reported in Table 2 (the amounts of VTMOEO and of hydophobic additives being expressed as % by weight with respect to the filler weight).

TABLE 2

SPECIMEN	VTMOEO (% weight)	HYDROPHOBIC ADDITIVE (% weight)	t (h)
REF. MIX. *	1.0	-	72
1*	2.0	-	96
2*	3.0	-	120
3*	1.0	2.0 STEARIC ACID	120
4	1.0	2.0 DYNASYLAN® 9116	216

REF. MIX. = Reference mixture;
1 = REF. MIX. + 2% VTMOEO;
2 = REF. MIX. + 3% VTMOEO;
3 = REF. MIX. + 2% stearic acid;
4 = REF. MIX. + 2% Dynasylan® 9116;
t = 1 kV for 30 min every 12 hours.

* = comparative;

[0068] From the above results, it is apparent that the silanes suitable for the cable of the invention, among the tested additives, allow to obtain the best results in direct current; further, it can be noted that such silanes are better than short chain silanes currently used, the amounts thereof being equal.

Claims

1. Self-extinguishing cable comprising at least one conductor and at least one flame-retardant coating, wherein the at least one flame-retardant coating comprises:

   a) at least one polymer material selected from: olefin homopolymers, olefin copolymers, copolymers of at least one olefin with at least one ethylenically unsaturated ester, polyesters, polyethers, polyether/polyester copolymers, and mixtures thereof;
   b) at least one inorganic hydrated flame-retardant filler;
   c) at least one silane substituted with at least one C_{10}-C_{40} hydrocarbon group and with at least one hydrolysable group.

2. A cable according to claim 1, wherein the polymer material is selected from:

   polyethylene; copolymers of ethylene with at least one α-olefin containing from 3 to 12 carbon atoms, and optionally with at least one diene containing from 4 to 20 carbon atoms; polypropylene; thermoplastic copolymers of propylene with ethylene and/or at least one α-olefin containing from 4 to 12 carbon atoms; copolymers of ethylene with at least one ester selected from alkyl acrylates, alkyl methacrylates and vinyl carboxylates, wherein the alkyl and the carboxylic groups comprised therein are linear or branched, and wherein the linear or branched alkyl group may contain from 1 to 8, preferably from 1 to 4, carbon atoms, while the linear or-branched carboxylic group may contain from 2 to 8, preferably from 2 to 5, carbon atoms; and mixtures thereof.

3. A cable according to claim 2, wherein the linear or branched alkyl group may contain from 1 to 4 carbon atoms, while the linear or branched carboxylic group may contain from 2 to 5 carbon atoms.

4. A cable according to any of the previous claims, wherein the polymer material is selected from copolymers of ethylene with at least one α-olefin containing from 3 to 12 carbon atoms, and optionally with at least one diene containing from 4 to 20 carbon atoms, obtained by single-site catalysis.

5. A cable according to any of the previous claims, wherein the inorganic hydrated flame-retardant filler is selected from: metal hydroxides, hydrated metal oxides, metal salts having at least one hydroxyl group, and hydrated metal salts.

6. A cable according to any of the previous claims, wherein the inorganic hydrated flame-retardant filler is a calcium, aluminium, magnesium or zinc hydroxide, hydrated oxide, salt having at least one hydroxyl group or hydrated salt.

7. A cable according to any of the previous claims, wherein the flame-retardant filler is selected from: magnesium hydroxide, alumina trihydrate, hydrated magnesium carbonate, hydrated calcium, magnesium carbonate, $4ZnO.B_2O_3.H_2O$, $2ZnO.3B_2O_3.3.5H_2O$, or mixtures thereof.

8. A cable according to any of the previous claims, wherein the flame-retardant filler is magnesium hydroxide.

9. A cable according to any of the previous claims, wherein the C_{10}-C_{40} hydrocarbon group contained in the silane is a C_{10}-C_{40} alkyl, alkenyl, aryl, alkylaryl, arylalkyl, arylalkenyl, alkenylaryl group, whereas the hydrolysable group is a C_1-C_{16} alkoxy group, optionally substituted by at least one C_1-C_{16} alkoxy group.

10. A cable according to any of the previous claims, wherein the C_{10}-C_{40} hydrocarbon group contained in the silane is a C_{12}-C_{24} alkyl, alkenyl, aryl, alkylaryl, arylalkyl, arylalkenyl, alkenylaryl group.

11. A cable according to any of the previous claims, wherein the silane has the following formula:

$$Y_{4-(x+z)}SiR_xR'_z \qquad (I)$$

wherein:

x is 1, 2 or 3; z is zero, 1 or 2; with the proviso that x+z is not higher than 3;
Y, equal or different from each other, are C_1-C_8 alkoxy groups, optionally substituted by at least one C_1-C_8 alkoxy group;
R, equal or different from each other, are selected from:
C_{10}-C_{40} alkyl groups, optionally substituted by at least one C_6-C_{14} aryl group;
C_{10}-C_{40} alkenyl groups, optionally substituted by at least one C_6-C_{14} aryl group;
C_6-C_{14} aryl groups, optionally substituted by at least one C_1-C_{30} alkyl group and/or by at least one C_2-C_{30} alkenyl group;
with the proviso that each of R has from 10 to 40
R', equal or different from each other, are selected from:
hydrogen;
C_1-C_{20} alkyl groups, optionally substituted by at least one C_6-C_{14} aryl group;
C_2-C_{20} alkenyl groups, optionally substituted by at least one C_6-C_{14} aryl group;
C_6-C_{14} aryl groups, optionally substituted by at least one C_1-C_{20} alkyl group and/or by at least one C_2-C_{20} alkenyl group.

12. A cable according to any of the previous claims, wherein the silane has the following formula:

$$Y_{4-(x+2)}SiR_xR'_z \qquad (I)$$

wherein:

x is 1, 2 or 3; z is zero, 1 or 2; with the proviso that x+z is not higher than 3;
Y, equal or different from each other, are C_1-C_4 alkoxy groups, optionally substituted by at least one C_1-C_4 alkoxy group;
R, equal or different from each other, are selected from:
C_{12}-C_{24} alkyl groups, optionally substituted by at least one C_6-C_{14} aryl group;
C_{12}-C_{24} alkenyl groups, optionally substituted by at least one C_6-C_{14} aryl group;
C_6-C_{10} aryl groups, optionally substituted by at least one C_1-C_{30} alkyl group and/or by at least one C_2-C_{30} alkenyl group;
with the proviso that each of R has from 10 to 40 carbon atoms;
R', equal or different from each other, are selected from:
hydrogen;

C_1-C_{16} alkyl groups, optionally substituted by at least one C_6-C_{14} aryl group;
C_2-C_{16} alkenyl groups, optionally substituted by at least one C_6-C_{14} aryl group;
C_6-C_{10} aryl groups, optionally substituted by at least one C_1-C_{20} alkyl group and/or by at least one C_2-C_{20} alkenyl group.

13. A cable according to any of the previous claims, wherein the silane has the following formula:

$$Y_{4-(x+z)}SiR_xR'_z \tag{I}$$

wherein:

x is 1, 2 or 3; z is zero, 1 or 2; with the proviso that x+z is not higher than 3;
Y, equal or different from each other, are C_1-C_4 alkoxy groups, optionally substituted by at least one C_1-C_4 alkoxy group;
R, equal or different from each other, are selected from:
C_{14}-C_{20} alkyl groups, optionally substituted by at least one C_6-C_{14} aryl group;
C_{14}-C_{20} alkenyl groups, optionally substituted by at least one C_6-C_{14} aryl group;
C_6-C_{10} aryl groups, optionally substituted by at least one C_1-C_{30} alkyl group and/or by at least one C_2-C_{30} alkenyl group;
with the proviso that each of R has from 10 to 40 carbon atoms;
R', equal or different from each other, are selected from:
hydrogen;
C_1-C_{12} alkyl groups, optionally substituted by at least one C_6-C_{14} aryl group;
C_2-C_{12} alkenyl groups, optionally substituted by at least one C_6-C_{14} aryl group;
C_6-C_{10} aryl groups, optionally substituted by at least one C_1-C_{20} alkyl group and/or by at least one C_2-C_{20} alkenyl group.

14. A cable according to any of the claims 11-13, wherein, in formula (I), x is 1; z is zero; Y, equal or different from each other, are selected from C_1-C_4 alkoxy group, optionally substituted by at least one C_1-C_4 alkoxy group; R is a C_{14}-C_{20} alkyl.

15. A cable according to any of the claims 11-14, wherein, in formula (I), x is 1; z is zero; Y, equal or different from each other, are selected from methoxy, ethoxy or methoxyethoxy group, optionally substituted by at least one methoxy, ethoxy or methoxyethoxy group and R is a hexadecyl or octadecyl group.

16. A cable according to any of the previous claims, wherein the silane is in an amount from 0.1% to 10% with respect to the total weight of the inorganic flame-retardant filler.

17. A cable according to any of the previous claims, wherein the silane is in an amount from 0.5% to 5% by weight with respect to the total weight of the inorganic flame-retardant filler.

18. Flame-retardant composition comprising: a) at least one polymer material; b) at least one inorganic hydrated flame-retardant filler; and c) at least one silane; a), b) and c) being defined according to any of the previous claims.

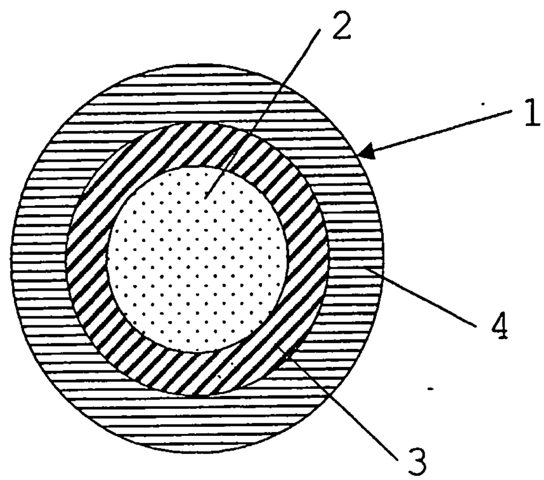


Fig. 1

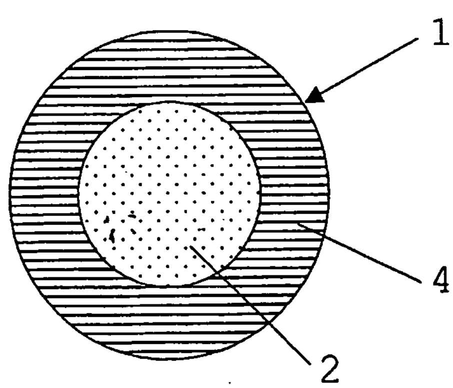
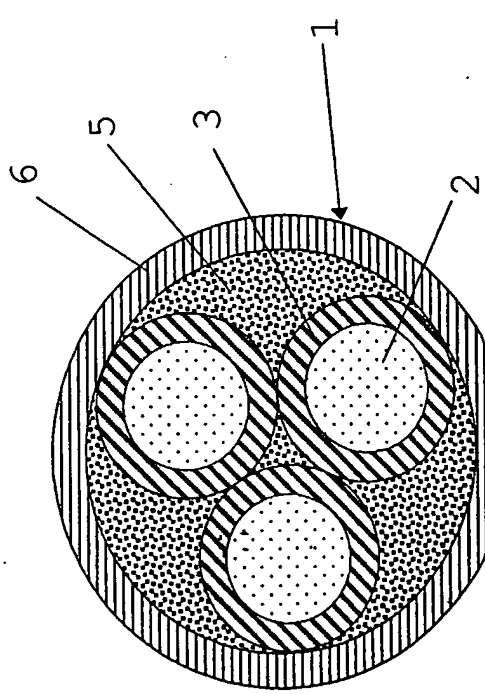


Fig. 2

Fig. 3



European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 01 12 1137

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	EP 0 520 752 A (BP CHEM INT LTD) 30 December 1992 (1992-12-30) * the whole document *	1-18	H01B7/295 H01B7/28 C08K3/22
A	US 5 412 012 A (BIGGS JAMES W ET AL) 2 May 1995 (1995-05-02) * the whole document *	1-18	

TECHNICAL FIELDS SEARCHED (Int.Cl.7)

H01B
C08K

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	29 January 2002	Drouot-Onillon, M-C

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 01 12 1137

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

29-01-2002

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
EP 0520752	A	30-12-1992	EP	0520752 A1	30-12-1992
US 5412012	A	02-05-1995	NONE		

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82